

acids among the volatile decomposition products. In one case a few grammes of the acid, contained in a miniature retort, were slowly heated in the paraffin bath, the volatile products being condensed in well-cooled tubes. Two distinct stages in the decomposition were observed. Just above the melting point the substance began to boil, giving off pungent-smelling vapors. The aqueous distillate had a strongly acid reaction, and on extracting it with ether and evaporating this solvent, a small quantity of needle-like crystals, having acid properties, was obtained. When the residue in the retort was heated to about 250° , renewed boiling, and more vigorous than before, took place. The distillate, which was of course separately collected, was oily and viscous, and was found to consist largely of an ether-soluble acid. It has not been prepared in sufficient quantity to permit an analysis. The ammonium salt crystallizes in little prisms, and its solution yields precipitates with calcium, barium, lead and silver salts. The lead salt deposits in beautiful stellated aggregates and seems very characteristic. The study of the decomposition products of dimethyl racemic acid will be continued as soon as enough of the starting material can be procured.

Central High School, Philadelphia,

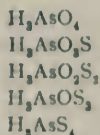
April 7, 1904.

TRISULPHOXYARSENIC ACID.

BY LEROY W. MCCAY.

(Read April 7, 1904.)

About eighteen years ago, in order to account for the irregularities accompanying the interaction of sulphuretted hydrogen and arsenic acid, I assumed the existence of three sulphyoxyarsenic acids lying between arsenic and sulpharsenic acid :



That the monosulphyoxyarsenic acid can exist in the free state I showed in 1886. A few months later Preis, of the University of

Prag, established the existence of the disulphoxyarsenic acid, and recently Dr. William Foster, Jr., and I have succeeded in preparing several salts of the trisulphoxyarsenic acid. Ever since Preis discovered the disulphoxyarsenic acid I have been convinced that the trisulphoxy-compound existed, and since it was the only acid necessary to complete the series, a great deal of experimental work was undertaken in order to isolate it.

Dr. Foster¹ published recently the results of an elaborate investigation of the action of magnesium oxide on a mixture of equivalent amounts of arsenic trisulphide and sulphur suspended in water, it being hoped that during the reaction the magnesium salt of the acid would be formed in sufficient amounts to make possible its transformation into the corresponding sodium salt, and the separation of this by means of alcohol. His work has served to clear up many matters bearing on the modes of formation of the sulphony-compounds; and although no perfectly consistent results were reached, sodium salts were prepared again and again whose composition approached so closely to one corresponding to the formula $\text{Na}_3\text{AsOS}_3 + 11\text{H}_2\text{O}$ that I felt convinced the substances were really impure tertiary sodium trisulphoxyarseniate.

A few preliminary experiments having established the fact that freshly precipitated arsenic pentasulphide suspended in water is decomposed far more readily by an excess of magnesium oxide than a mixture of equivalent amounts of arsenic trisulphide and sulphur, I suggested to Dr. Foster that we conjointly make a careful examination of the resulting solution. The proposal was a profitable one, for we find that the solution contains large quantities of magnesium trisulphoxyarseniate.

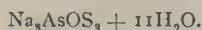
The magnesium salt of trisulphoxyarsenic acid, then, is formed when magnesium oxide in excess acts upon freshly prepared arsenic pentasulphide suspended in water kept during the entire reaction at 0°C . The change is rather slow, when the amount of arsenic pentasulphide is large, but it is generally complete in four to five hours.

By precipitating the magnesium in solution by means of sodium hydroxide, as magnesium hydroxide, adding an equal volume of alcohol to the filtrate from the magnesium oxide and hydroxide, and keeping the corked flask and its contents in the ice chest, the

¹ *Z. anorg. Chem.*, 37, 64 (1903).

tertiary sodium salt of the acid commences to separate out in feathery crystals which, in the course of twelve hours, pass over into fine fern-like forms. The compound is purified by recrystallization. The yields are very satisfactory. Thirty grams of As_2S_5 yield about thirty grams of the impure salt.

The compound possesses a composition represented by the formula



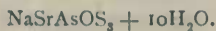
	<i>Calculated.</i>	<i>Found.</i>
Na.....	15.22%	15.65%
As.....	16.50 "	16.84 "
O.....	3.52 "	3.45 "
S.....	21.16 "	20.74 "
H ₂ O.....	43.60 "	43.32 "
	<hr/> 100.00	<hr/> 100.00

The tertiary potassium salt is prepared in an analogous manner. On the addition of the alcohol it separates out in the form of a light yellow oil, which, however, solidifies to a straw-colored, crystalline mass when kept for some hours at -20°C .

It crystallizes with seven molecules of water :



By adding an alcoholic solution of strontium chloride to an aqueous solution of the sodium salt, the double trisulphoxyarsenate of sodium and strontium is precipitated in a crystalline condition :

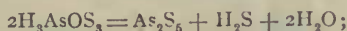


Barium chloride produces in a solution of the tertiary potassium salt a crystalline precipitate of potassium barium trisulphoxyarsenate :

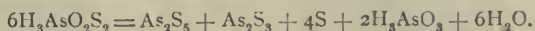


Aqueous solutions of sodium trisulphoxyarsenate are not precipitated by strontium chloride. This reaction has been made use of for separating the small amount of monosulphoxy-salt which is occasionally thrown down along with the trisulphoxy-compound. Barium chloride precipitates both the di- and trisulphoxyarsenic acids, but the barium salt of the latter acid is more soluble than that of the former. The behavior of these two acids toward hydrochloric acid is also a means of distinguishing between them.

If a dilute solution of sodium trisulphoxyarsenate be treated with enough acid to render it strongly acid, then shaken violently and filtered, the filtrate is clear and becomes but faintly turbid on boiling. If a dilute solution of sodium disulphoxyarsenate of the same concentration be tested in a similar way, the filtrate becomes strongly turbid on boiling. When these tests are made in flasks and the flasks, immediately after the addition of the hydrochloric acid, are stoppered, so as to prevent the escape of the sulphuretted hydrogen, at the end of thirty-six hours no smell of the gas can be detected in the flask which contained the disulphoxy-salt, while it is still very pronounced in the one which contained the trisulphoxy-compound. These two reactions have been studied very carefully. It appears that the trisulphoxy-acid breaks down as follows :



the disulphoxy-compound thus :



The three sulphoxyarsenic acids are not precipitated at once by Weinland's¹ reagent, which fact serves to distinguish them from sulpharsenic acid. All three can be readily separated from arsenic acid by means of magnesia mixture which precipitates only the latter. The formation of these three sulphoxyarsenic acids, their instability and the products of their decomposition, account in a perfectly rational manner for all the irregularities accompanying the interaction of sulphuretted hydrogen and arsenic acid. This is a summary of our work so far as it has thus far progressed.

Princeton, N. J., April 4, 1904.

¹ An aqueous solution of tartar emetic and Rochelle salt.